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# GAUGE-INVARIANT ATOMIC ORBITAL CALCULATIONS OF INTRAMOLECULAR CHEMICAL SHIFTS DUE TO MOLECULAR FRAGMENTS

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ABSTRACT

Calculations of intramolecular influences on the changes of proton chemical shifts have been carried out for cyclohexane, 1,3-dioxane, 1,3-dithiane, sulfite and phthalylsulfite, with the aim of understanding the observed trends and application to conformational studies by NMR spectroscopy. The wavefunctions of molecular model fragments distinguishing one molecule from another have been calculated using the SCF method at the STO-6G level. The approach of gauge-invariant atomic orbitals is used to evaluate the perturbation of a molecular system by a magnetic field. Chemical shift changes are in agreement with the available experimental data.

## INTRODUCTION

Understanding the nature of nuclear magnetic shielding is of fundamental importance since it reflects the slightest changes in the electronic and spatial structure of a molecule. By studying the NMR spectra of various nuclei in a given molecule it is possible to obtain intimate information about the conformational peculiarities due to intramolecular interactions. In order to extract information about molecular structure from experimental data and to identify spectral lines with specific protons it is necessary to carry out theoretical calculations of magnetic shielding constants. The appropriate theory has been known for over 30 years but significant progress in magnetic shielding calculations has been made only with the recent acquisition of improved computer facilities and improved theoretical approaches. Within the framework of the coupled SCF perturbation theory using very large and flexible basis sets, reasonably good results have been obtained for a number of small molecules [1,2]. Ditchfield has developed a theory which utilizes a basis set of gauge-invariant atomic orbitals (GIAO) within the perturbed Hartree–Fock framework and which has been successfully applied to magnetic shielding calculations of small molecules with the use of moderate-size basis sets [3, 4]. In this procedure each molecular orbital is expressed as a linear combination of atomic orbitals

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